SULPHUR ISOTOPES IN METEORITES
AND SEA WATER SULPHATES

THE ISOTOPIC COMPOSITION OF
SULPHUR IN METEORITES
AND SEA WATER SULPHATES

By

John Edmund Warren, B.Sc.

A Thesis
Submitted to the Faculty of Arts and Science
in partial fulfilment of the requirements
for the degree
Master of Science

McMaster University,
October, 1954.

MASTER OF SCIENCE (1954)
(Physics)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: The Isotopic Composition of Sulphur in Meteorites and Sea Water Sulphates.

AUTHOR: John Edmund Warren, B. Sc. (McMaster University)

SUPERVISION: Professor H. G. Thode

NUMBER OF PAGES: vi, 47

SCOPE AND CONTENTS:

The isotopic composition of meteorite sulphur and sea water sulphates was investigated by means of a simultaneous collection mass spectrometer. It was found that sixteen samples of meteoritic sulphur possessed identical isotope abundances within the precision of the instrument. The sulphates from various depths in the Atlantic, Pacific and Arctic Oceans, were found to be enriched in S^{34} compared to the meteoritic base level. The overall variation in S^{32}/S^{34} content was 0.39 percent for the sea water samples.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor H. G. Thode for his kind aid, advice and direction in this investigation. The author would also like to thank Drs. N. Nininger, E. P. Henderson, R. Wallouch, W. Fleming, and Mr. A. Harrison, for their generous cooperation and aid.

The financial assistance of the Research Council of Ontario is gratefully acknowledged.

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INTRODUCTION

Research carried on in this laboratory has revealed widespread variations in the isotopic composition of terrestrial sulphur. The average composition of such samples is extremely close to that of meteoritic sulphur, indicating the primordial abundance of these isotopes is that of sulphur in meteorites. Consequently, it is of the utmost importance to know as accurately as possible the value of the isotopic composition of such sulphur and the uniformity of the value. Sulphur from eighteen meteorites has been studied with this view in mind.

It has been found that relative to meteoritic sulphur, sulphides are depleted in S^{34} while sulphates are enriched in this isotope. Since a considerable part of this fractionation has occurred through oxidation-reduction processes which go on in the sea, it is necessary in the interpretation of sulphur isotope fractionation studies to know the isotope ratio and its uniformity for present day sea water sulphate. As a consequence, sea water samples have been obtained from various depths in the Atlantic, Pacific and Arctic Oceans and the isotopic composition of the sulphates measured.

Historical

The discovery of radioactivity in uranium by Becquerel (1) in 1896 opened a new era of intensive research into the nature of the atom. Later, Soddy (2) and independently Fajans (3) found that isotopes existed among the radioactive elements and Soddy concluded that they might exist throughout the periodic table; J. J. Thomson (4), with his first crude mass spectrograph gave this idea visible proof by showing that neon consisted of a least two isotopes of masses 20 and 22.

Because of this discovery, a number of investigators sought to find small variations in the measured atomic weights of elements due to slight variations in the abundances of the isotopes. At first the search was fruitless because of the lack of precision, the use of light elements whose heavier isotopes are rare and heavy isotopes whose isotopic abundances are nearly constant. At last Briscoe (5), in 1925 reported slight variations in the atomic weight of boron depending on the geological position of the deposit from which the sample was taken. He explained the differences in terms of variations in the abundances of the boron isotopes.

The rare isotopes of the light elements that had escaped detection in early mass spectrograph studies were discovered by means of molecular spectra. In the molecular spectra of homopolar molecules, there was an alteration of intensities of the band lines which could only be explained by assuming the presence of a rare isotope as well as the presence of the known one. By this method, four rare isotopes were discovered in 1929, O^{17} and O^{18} by Giaque and Johnston (6), C^{13} by King and Birge (7) and N^{15} by Naude (8).

Birge and Menzel (9) were first to predict that hydrogen should have a rare isotope of mass two, to the extent of about one part in forty-five thousand. It was left to Urey and his co-workers to show that it existed and could be separated by the distillation of liquid hydrogen. Later, Washburn and Smith (10) found that the vapour pressure of H_2O and D_2O differed from each other and by electrolysis and distillation the isotopes could be separated. The early experiments provided the first proof that isotopes do not possess identical physical properties.

Later a theoretical basis for differences in chemical and physical properties was established. By means of statistical mechanics Urey and Rittenburg (11) calculated the exchange of hydrogen and deuterium in molecular hydrogen and the hydrogen halides. The equilibrium constants were greater than unity indicating that in certain reactions, isotopic fractionation would occur. This was also found to be the case for exchange reactions involving the isotopes of lithium, boron, carbon, nitrogen and oxygen (12). Urey and his co-workers (13, 14) carried out experimental work to prove the validity of these calculations. Since the equilibrium constants for certain reactions do differ from unity, it becomes apparent that isotopes differ in thermodynamic properties and consequently fractionation results in naturally occurring equilibrium processes.

Variations in the abundances of isotopes have been and are being studied by investigators with the hope that the results will help to explain many geological, biological and chemical phenomena. One of the first elements to come under this investigation was oxygen. Emeleus (15) observed that the density of water taken from different places was not constant and thought that this explained the larger and smaller amounts of deuterium present. It soon became apparent that this was only a partial explanation and that the variation of the oxygen isotopes profoundly effected the density. Following these results, Dole and his co-workers (16-21), made a comprehensive survey of these isotopes in air, water and minerals by means of sensitive density methods. They detected up to four percent variations in the O^{18} content of these substances.

With the advent of precision mass spectrometry these early results were confirmed. Thode and Smith (22) did an oxygen survey and found a four percent spread in values. Later Baertschi and Silverman (23-25) using the same technique, carried on these investigations and found that the O^{16}/O^{18} ratio varied by as much as two percent and that the O^{18} content was greater for sedimentary rock than for igneous rock.

A great deal of work has been done on the abundances of the carbon isotope in nature. Nier and his co-workers (26-27) found variations up to five percent with limestones and inorganic material enriched to C^{13} while organic matter showed a depletion. Mars (28) and Trofimov (29) doing similar research confirmed their results. Wickman (30-31) investigating the C^{13}/C^{12} ratio in a large number of plants, found that the ratio remained constant among plants grown in different environments. Recently, Harmon Craig (32) has published a comprehensive survey of carbon isotopes in organic and inorganic material. His results agree very well with those of previous investigators. Carbonate rocks were found to be enriched by about two percent in C^{13} while marine carbon was enriched by one percent compared to terrestrial organic carbon.

However, atmospheric CO_2 was found to be richer in C^{13} than previous experiments had revealed. He could find no correlation between the C^{13}/C^{12} ratio and the age of fossil wood, coal and limestone.

A number of other elements have been studied with regard to their isotopic abundances. Thode et. al., (33) showed that the isotopic composition of boron varied as much as 3.5 percent while Macnamara (34) revealed that there existed a 1.5 percent spread in the B^{11}/B^{10} ratio in samples from different boron deposits of California. Graham, Macnamara, MacFarlane and Crocker (35), taking germanium from a variety of locations, found a 0.7 percent variation in the isotopic abundances. This was the first experimental evidence that fractionation occurs in isotopes of the higher masses. Recently, Edwards (36) reported a 0.5 percent difference in the Cl^{35}/Cl^{37} ratio of Halite samples from two different salt deposits. Reynolds and Verhoogen (37) investigating silicon in rocks and minerals found the Si^{30} content decreased from a high-temperature mineral (olivine) to a low-temperature pegmatite quartz, to vein quartz, to geyserite.

Sulphur

In 1927 Aston (38) showed that sulphur was in reality a mixture of at least three isotopes of masses 32, 33 and 34 and gave as the abundances 96:1:3. Later

Nier (39) found in naturally occurring sulphur, another isotope of mass 36 and gave the abundances of the known isotopes good to two percent, as,

Atomic Mass	32	33	34	36
Abundance percent.	95.1	0.74	4.2	0.016

Unfortunately, the source of the sulphur used is unknown other than that it was commercial sulphur dioxide.

Next to titanium, manganese and phosphorous, sulphur is the most abundant of the trace elements in the upper parts of the lithosphere. It is a universal constituent of plants in the form of inorganic sulphates, organic sulphides and proteins. It also occurs in many terrestrial compounds such as gypsum and anhydrite, metallic sulphides, native sulphur and hydrogen sulphide gas and in meteorites as iron sulphide.

Since there is a large percentage mass difference between the isotopes S^{32} and S^{34}, it was to be expected that the sulphur isotopes would differ in their chemical and physical properties. Consequently, through many processes that occur in nature, the sulphur isotopes would be fractionated and wide variations exist in the abundances of its isotopes in terrestrial substances. Because of this, sulphur became of great interest to investigators in the hope that research into its isotopic composition would reveal some of the processes through which many natural substances have passed during

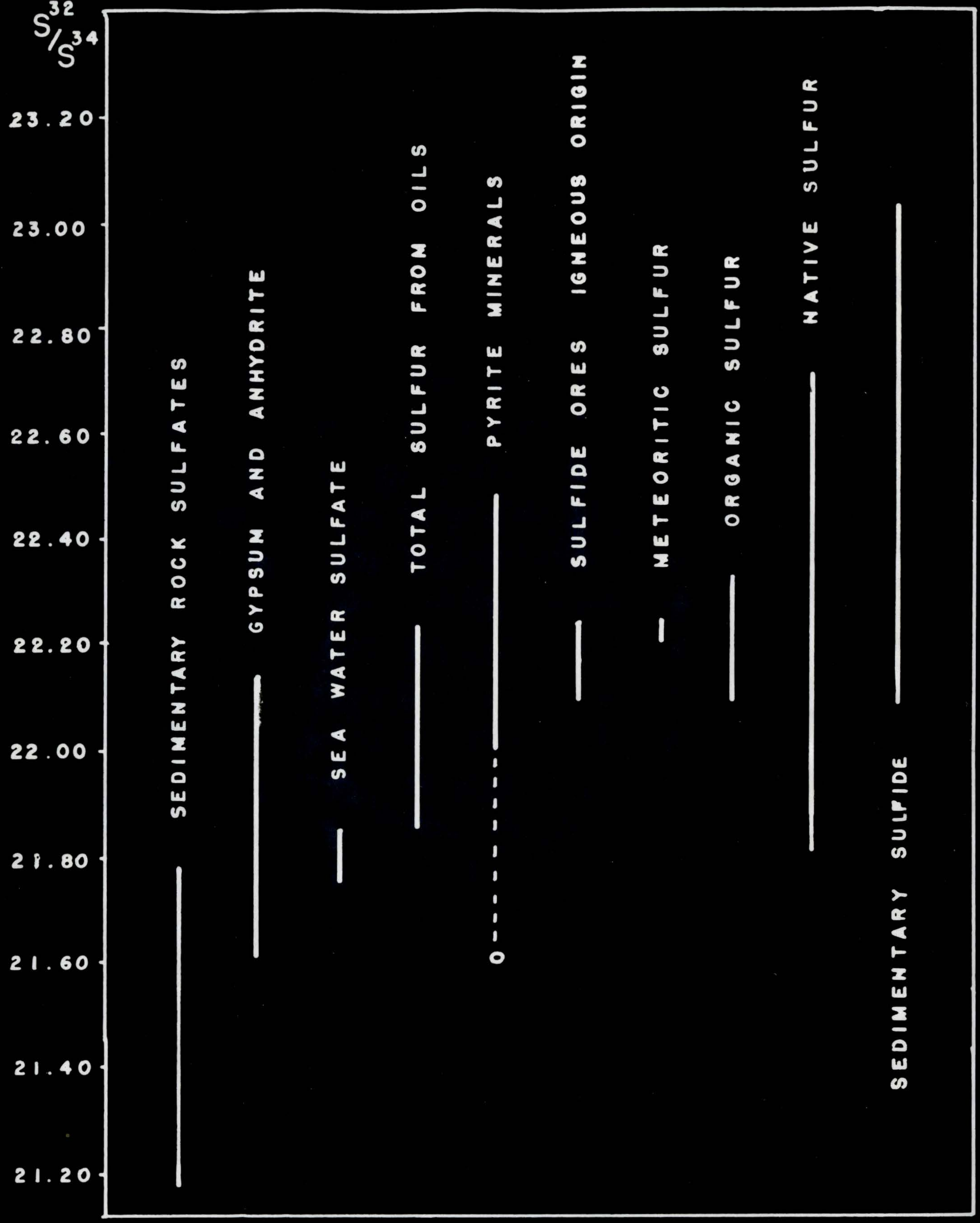


FIG I

DISTRIBUTION OF S^{34} IN TERRESTRIAL AND METEORITIC SULFUR and since their formation. With this end in view, such a study was undertaken in this laboratory in 1947.

The results so far obtained are summarized in Figure I. It can be seen that the concentration of S^{34} varies by as much as nine percent depending on the source of sulphur. In general, it has been found that the sulphates are enriched in S^{34} while the sulphide and hydrogen sulphide gas are depleted in the isotope relative to meteoritic sulphur.

Macnamara and Thode (40) have reported that meteoritic sulphur possesses an exceedingly constant isotopic composition. The S^{32}/S^{34} ratios of these samples lie midway between the ratios of terrestrial sulphur, suggesting that the primordial sulphur is that now found in meteorites. After the earth's formation, this element in the earth's crust has undergone fractionation through biological processes which meteorites have escaped. Consequently, the isotopic composition of meteoritic sulphur has been taken as the base level for comparison.

It is apparent from the graph that sulphides of igneous origin are slightly more enriched in S^{34} than meteoritic sulphur. Organic sulphur has a range of S^{32}/S^{34} values above and below the meteoritic, while native sulphur of volcanic and organic origin has a spread of 4.0 percent, about half the samples showing an enrichment in S^{34} and half a depletion compared to the base level.

Sulphates in sedimentary rock, gypsum and anhydrite have S^{32}/S^{34} ratios which extend from the meteoritic base level to a 4.7 percent enrichment in the heavy isotope. Sedimentary sulphides on the other hand show a similar spread but in the opposite direction, i.e., a depletion in the heavy isotope.

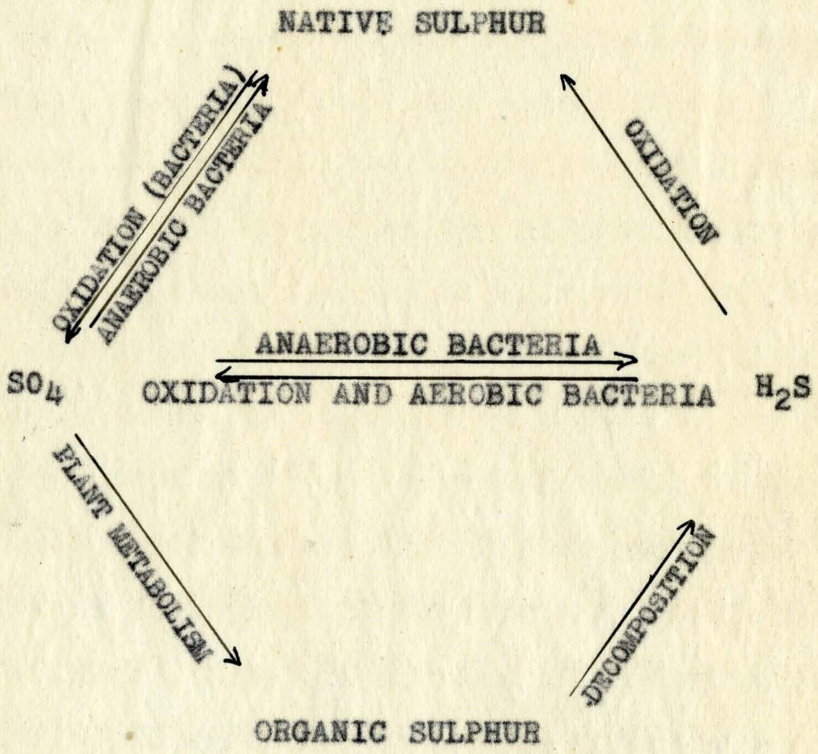
<u>The Sulphur Cycle</u>

It is evident from these isotope distribution studies that the sulphur isotopes have been fractionated through geological and chemical processes which occur in nature, and involve the oxidation and reduction of sulphur. It is expected that fractionation takes place by means of the following exchange reaction,

$$S^{32}O_4^= + H_2{}^{34}S \rightleftarrows S^{34}O_4^= + H_2S^{32}$$

where at equilibrium the heavy isotope is favoured in the sulphate ion by about 7.5 percent at 25° C. This is the approximate spread found between sulphides and sulphates in natural substances today which probably indicates that equilibrium is gradually being established in nature.

However, the sulphate ion will not reduce unless provided with a great deal of energy and under normal conditions sulphates will not exchange their sulphur with hydrogen sulphide. It has been suggested that the biological sulphur cycle in the sea outlined below, provides the mechanism by which this exchange process can occur. Certain parts of the sulphur cycle have been examined under controlled conditions in the laboratory. Thode, Kleerekoper and McElcheran (41) found that the hydrogen sulphide produced by the bacterial reduction of sulphate was depleted by one percent at 25° C in S^{34} compared to the source sulphate.



More recently, Wallouch et al., (42), have found that the amount of fractionation is increased at lower temperatures (two percent at 10° C). Also Feely, Gast and Kulp (1953), (43), have confirmed fractionation factors of this order of magnitude.

As it can be seen from the diagram, of the sulphur cycle, native sulphur is an important intermediate. Free sulphur found in the mud at the bottom of lakes in Africa, formed by the bacterial reduction of sulphate to hydrogen sulphide and by purple bacteria to free sulphur, is depleted by as much as 3.2 percent in the heavy isotope compared to the sulphate (44). While this amount is about half what would be expected if isotopic equilibrium had been established, nonetheless, it is large and in the correct direction.

Further evidence that the sulphur cycle is one mechanism under which the sulphur isotopes are fractionated in natural processes, has been obtained in this laboratory. Thode, Wanless and Wallouch (45) carried out sulphur and carbon isotope abundance studies on sulphur well cores and adjacent formations in the Texas and Louisiana salt domes. They obtained abundance data on sulphate, free sulphur and sulphide present in eleven different well cores from ten different sulphur wells. It was found that the sulphur is depleted in S^{34} with respect to the sulphate by 3.9 percent on the average and the sulphide is further depleted by about one percent. The same study was made on the gypsum and anhydrite layers adjacent to calcitic sulphur bearing limestone but here little evidence of fractionation was found.

When sulphate is reduced to hydrogen by bacterial action, organic matter must be present to provide a source of free energy. Evidence of organic matter is found in the well cores and it is felt that the calcite layer was formed from this matter when the reduction of sulphate to sulphide occurred. Recently, Harmon Craig (32) examined the C^{13}/C^{12} ratio in plants, coal and petroleum and found these were depleted in the heavy isotope, compared to his standard. Consequently, calcite formed from organic matter would be depleted in this isotope. Thode, using the same standard found that calcitic layer of the sulphur wells was depleted in C^{13} by as much as 3.3 percent to 5.5 percent. Hence, it appears that the sulphur present in the sulphur wells of Texas and Louisiana was formed by bacterial reduction of sulphate and in the process, organic matter was transformed to calcite.

Other evidence of the sulphur cycle creating a spread in the isotopic composition of sulphur has been observed by Thode, Fleming and Macnamara (46). It appears that the isotopic abundances of sulphides

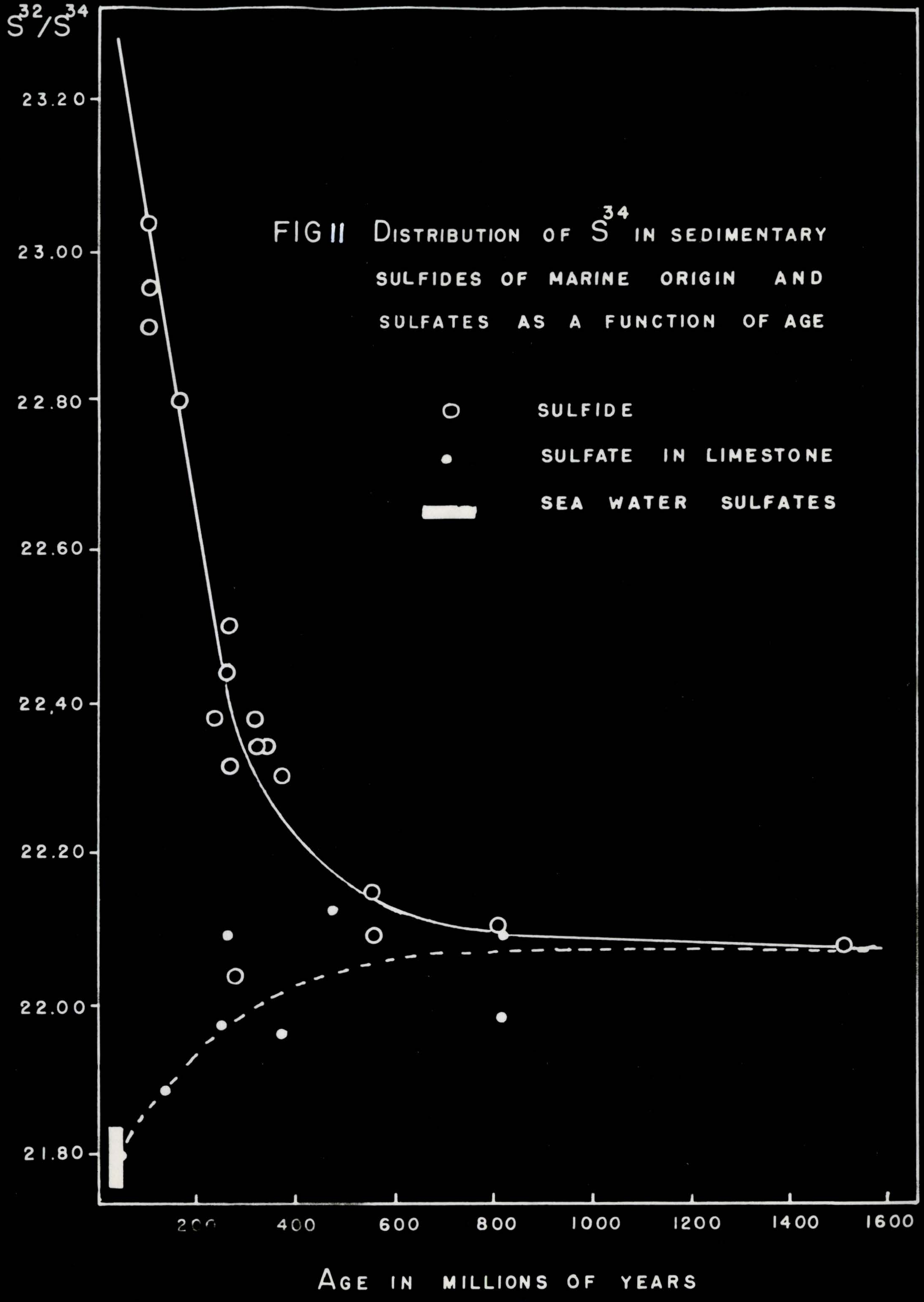


FIG II Distribution of S^{34} in sedimentary sulfides of marine origin and sulfates as a function of age found in sedimentary rock can be correlated with their geological age. It can be seen from Figure II that previous to about eight hundred million years ago, little or no spread in the S^{32}/S^{34} ratios is apparent between sulphides of sedimentary origin or meteorites. From that time on fractionation has taken place at an even increasing rate until the present day when the spread in concentration of S^{34} between sea water sulphate and recently deposited sulphides is about 7.4 percent. This would seem to indicate that isotopic equilibrium between sulphates and sulphides is being established slowly through geological time by means of the sulphur cycle. Since no fractionation occurred previous to eight hundred million years ago, it appears that little or no life involving sulphur was present. From that time such life has become more and more abundant allowing the sulphur cycle to operate and fractionation of sulphur isotopes to take place.

While it is important to know the present values of the S^{32}/S^{34} ratios for sea water sulphates from which sedimentary sulphides were formed, it is even more important to know if sulphates from the different oceans and different depths have a uniform sulphur composition. If sulphates are uniform today then it is highly probable that they have been uniform throughout geological history, even though the value of the S^{32}/S^{34} ratio may have been gradually changing over the years. Consequently, samples of sea water have been obtained from a variety of depths in the Atlantic, Pacific and Arctic Oceans and the sulphates analysed.

Similarly meteoritic sulphur has been accepted to be primordial sulphur, the base from which all fractionation of terrestrial sulphur has taken place. It thus becomes essential to know within what limits the S^{32}/S^{34} ratio of sulphur in meteorites is constant. With this end in view, several new meteorities and some previously analysed samples were studied. The results of the analysis of sea water sulphate and meteoritic sulphur are reported in this thesis.

Theoretical

Isotope Exchange Reactions: By means of statistical mechanics, equilibrium constants for isotope exchange reactions can be calculated. Urey and Grieff (47) first showed that these constants for reactions involving the isotopes of light elements differed from unity. Recently Tudge and Thode (48) made similar calculations for sulphur and found, for reactions involving S^{32} and S^{34} that the calculated equilibrium constants varied from 1.000 to 1.096. Consequently, appreciable fractionation would be expected in such processes in nature and in the laboratory.

The method for calculating equilbrium constants by finding the partition function ratios of isotopic molecules is as follows. In general, the exchange reaction is,

$$a\,A_1 + b\,B_2 \rightleftarrows a\,A_2 + b\,B_1 \qquad (1)$$

where A and B are molecules which have one element in common, subscripts 1 and 2 indicate that the molecules contain only the light or heavy element. It is known that for any reaction, the equilibrium constant K is given by,

$$-RT \ln K = \Delta F^o \qquad (2)$$

where F^o is the standard free energy of the reaction under study. Thus for the typical exchange process,

$$-RT \ln K = a\,F^o_{A_2} + b\,F^o_{B_1} - a\,F^o_{A_1} - b\,F^o_{B_2} \qquad (3)$$

The partition function Q is defined by the formula,

$$Q = \sum_{i=0}^{\infty} g_i \; e^{-\varepsilon_i/kT} \qquad (4)$$

where g_i is the number of quantum states with nearly equal energy, ε_i the energy of the state, k Boltzmann's constant, and T the absolute temperature.

Now the free energy is related to the partition function by the following equation,

$$F = E_o + R\,T \ln N - R\,T \ln Q \qquad (5)$$

where E_o is the zero point energy of the molecule and N is Avogadro's number. Substituting (5) in (4) and simplifying K becomes,

$$K = \left[\frac{Q_{A_2}}{Q_{A_1}}\right]^a \bigg/ \left[\frac{Q_{B_2}}{Q_{B_1}}\right]^b \; e^{\frac{-a\,E_{oA_2} - bE_{oB_1} + aE_{oA_1} + bE_{oB_2}}{R\,T}} \qquad (6)$$

Now instead of taking E_o as the "zero point energy" it can be taken as the bottom of the "potential energy curve" for the molecule. Since potential energy curves are taken to be identical for isotopic molecules, E_{oA_2} equals E_{oA_1}, and E_{oB_2} equals E_{oB_1}. Thus, equation (6) reduces to,

$$K = \left[Q_{A_2}/Q_{A_1}\right]^a \bigg/ \left[Q_{B_2}/Q_{B_1}\right]^b \qquad (7)$$

Therefore, in order to calculate the equilibrium constant for a specific exchange reaction, it is necessary only to determine the ratio of the partition functions of A and B. The ratio Q_2/Q_1 for a diatomic chemical compound can be found from the equation.

$$Q_2/Q_1 = \frac{l_2\, 6_1\, M_2^{3/2}\; e^{-u_2/2}\; (1 - e^{-u_1})}{l_1\, 6_2\, M_1^{3/2}\; e^{-u_1/2}\; (1 - e^{-u_2})} \qquad (8)$$

where l_2 and l_1 are the moments of inertia of the isotopic molecule, 6_1 and 6_2 are the symmetry numbers,

M_2 and M_1 are their molecular weights and u_2 and u_1 are related to the fundamental vibrational frequencies by relations of the kind $u_i = hc\omega_i/kT$.

Unidirectional Processes: Fractionation of isotopes will occur in chemical reactions if the reaction rates of the isotopic species involved are different. Eyring (49) has derived formulae from which the ratio constants for reactions of isotopic molecules can be calculated. More recently, Bigeleisen (50) has developed an expression for the ratio of the rate constants, which is more convenient and gives a greater insight into the significant factors.

Consider reactions between A_1, B, C, . . . to give P_1 and A_2, B, C, . . . to give P_2 where A_1 and A_2 are isotopic molecules of elements other than hydrogen. The ratio constants is,

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \; \frac{C_1^*}{C_2^*} \; \frac{C_{A_2}}{C_{A_1}} \; \left[\frac{M_2^o}{M_1^o}\right]$$

where K is the transmission coefficient, C is the concentration of the activated complex, M^o is the effective mass of the complex along the coordinates of decomposition. The ratios of the concentrations of the individual molecules can be replaced by the corresponding partition function ratios. Thus,

$$\frac{k_1}{k_2} \quad \frac{K_1}{K_2} \quad \frac{Q_{1*}}{Q_{2*}} \quad \frac{Q_{A_2}}{Q_{A_1}} \quad \left[\frac{M_2^{\circ}}{M_1^{\circ}}\right]^{1/2}$$

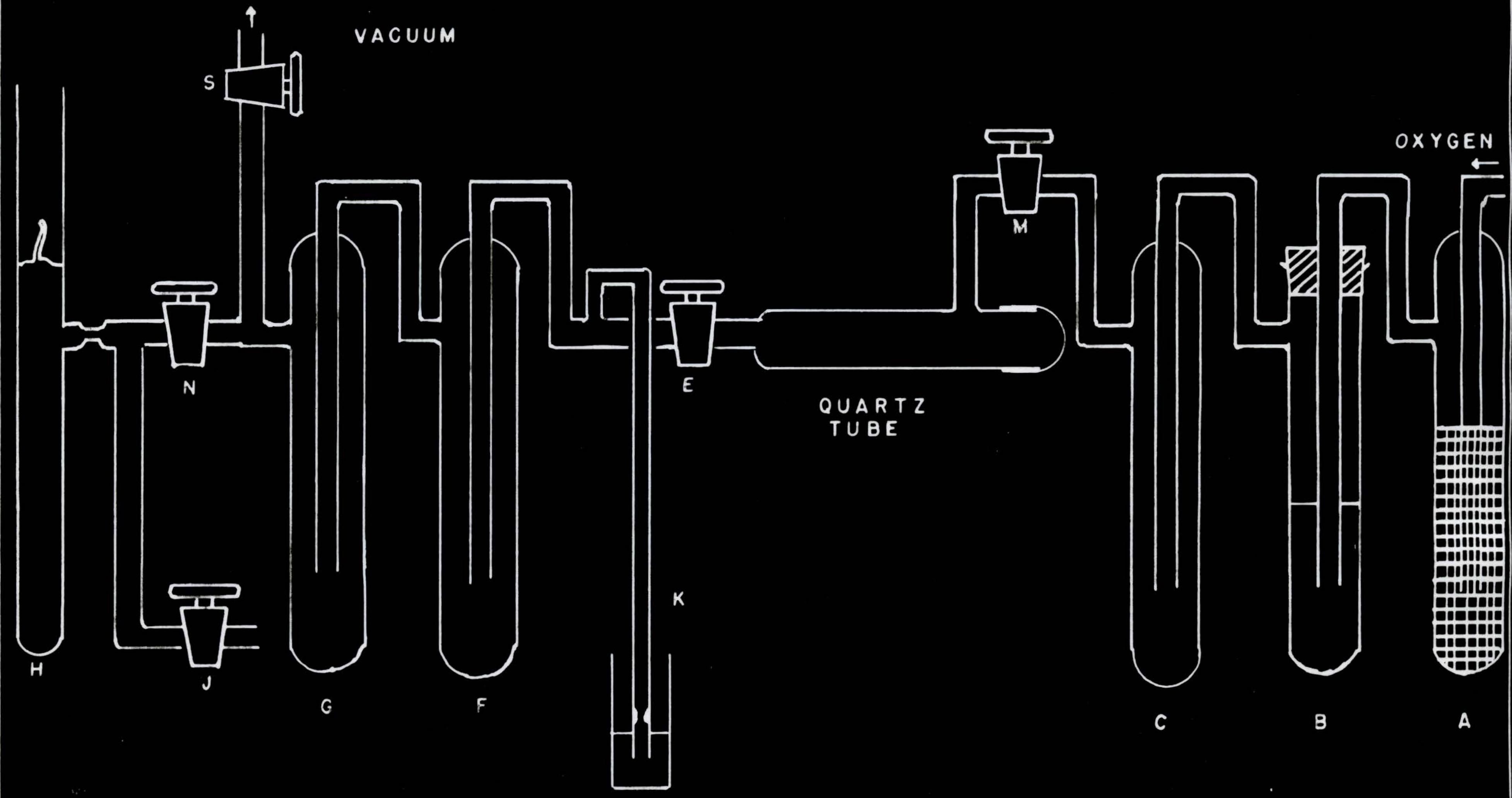
Bigeleisen and Mayer (51) using the above results, have obtained the following equation,

$$\frac{k_1}{k_2} \quad \frac{S_1 S_{2*}}{S_2 S_{1*}} \quad \frac{M_2^{\circ}}{M_1^{\circ}} \quad ^{1/2}\left[1+\sum_{i}^{3n-6} G(u_i)\,\Delta u_i - \sum_{i}^{3n'-6} G(u_i)^{*}\,\Delta u_i^{*} \right]$$

where S is a symmetry number, $G(u)$ is a free energy function, 3n-6 is the number of vibrational modes in the molecules, and u_i as before, is equal to $\frac{hc w_i}{kT}$. By definition subscripts 1 and 2 refer to the light and heavy molecules, respectively. The superscript $^{\circ}$ refers to a property of the transition state. The factor involving the S's has a statistical nature, if two or more identical atoms of the isotope are contained in the molecule, there will be an increase in the probability of one of them reacting. The factor $M_2^{\circ}\ M_1^{\circ}\ ^{1/2}$ gives the ratio of the number of light and heavy "activated complexes" which decompose per unit time. The quamtity in the square bracket gives a quantitative description of the effect of the differences in the zero point energies of the light and heavy molecules in the normal and transition states.

Provided the mechanism and the necessary partition functions are known, the amount of isotopic fractionation for any process can be calculated.

So far, agreement between theory and experiment has been good.



COMBUSTION TRAIN FIG III

EXPERIMENTAL

Meteorites

In most cases the meteorites studied in these experiments possessed showings of troilite (Fe S) which were removed from the meteorite and converted to sulphur dioxide for analysis in the mass spectrometer. However, certain fragments of meteorites were obtained which contained no visible troilite. Consequently, these fragments had to be pulverized to a fine powder in preparation for combustion.

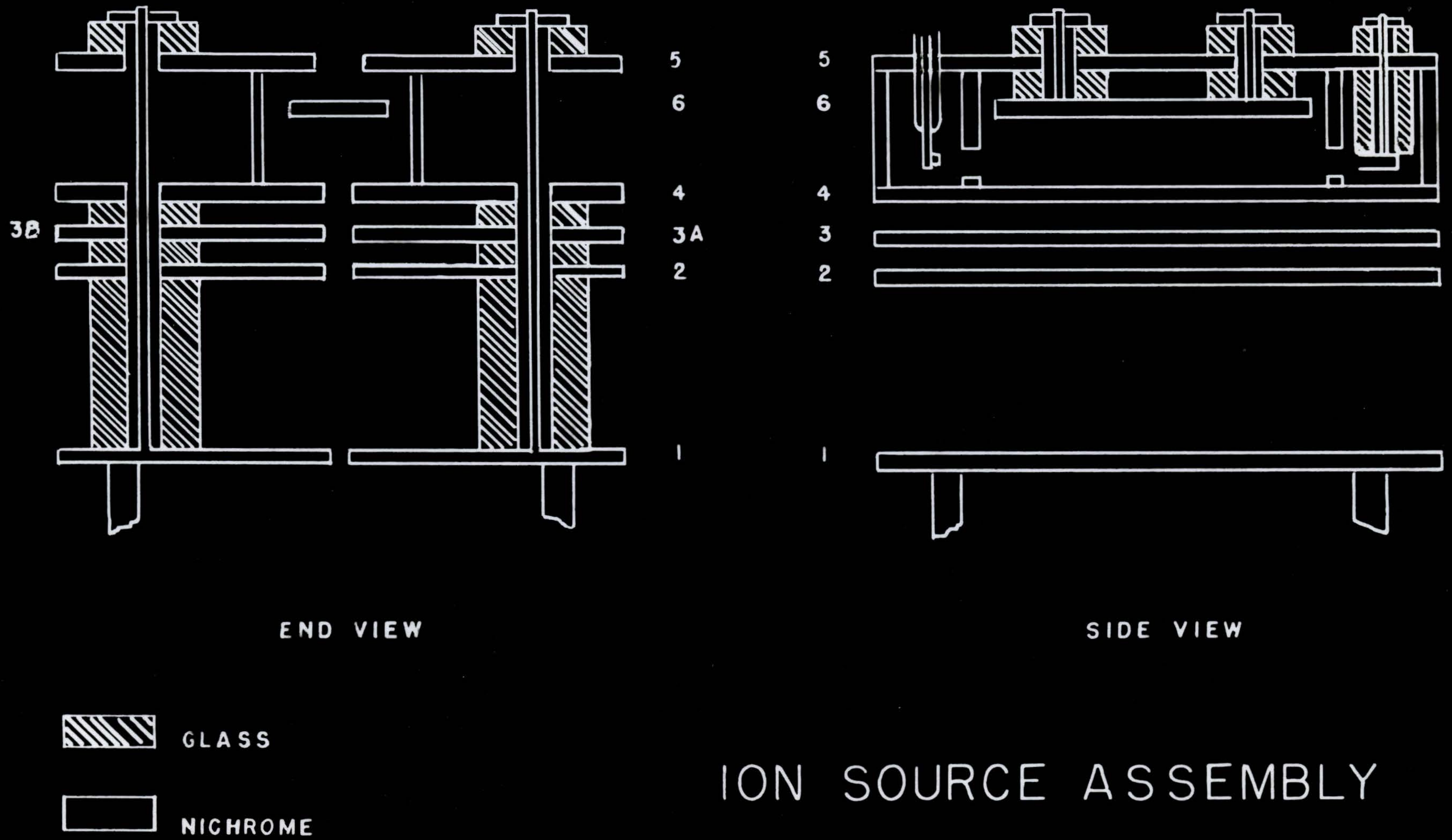
The apparatus used to burn the iron sulphide, illustrated in Figure III, consisted of three parts, an oxygen purifying train, a quartz combustion tube and a collection line.

The oxygen, which came from the same source for all analyses, was purified by passing through a dry ice and acetone bath. From there it bubbled through concentrated sulphuric acid in trap B and then into C the liquid air trap. This process is assumed to remove the moisture and hydrocarbons present.

Each specimen of troilite was placed in a clean nichrome boat and the boat inserted in the quartz combustion tube. The train was then evacuated and the collection line flamed to drive out moisture and residual sulphur dioxide on the glass walls. The line was brought up to atmospheric pressure with the purified oxygen and the troilite heated. On conclusion of the reaction, the system was again evacuated, then the pumps shut off and the frozen sulphur dioxide allowed to vapourise. The SO_2 was frozen down once more and pumped. In this way non-condensible gases formed during combustion and trapped in the frozen dioxide are removed. After this the SO_2 was caught in sample tube H and the tube was removed from the line.

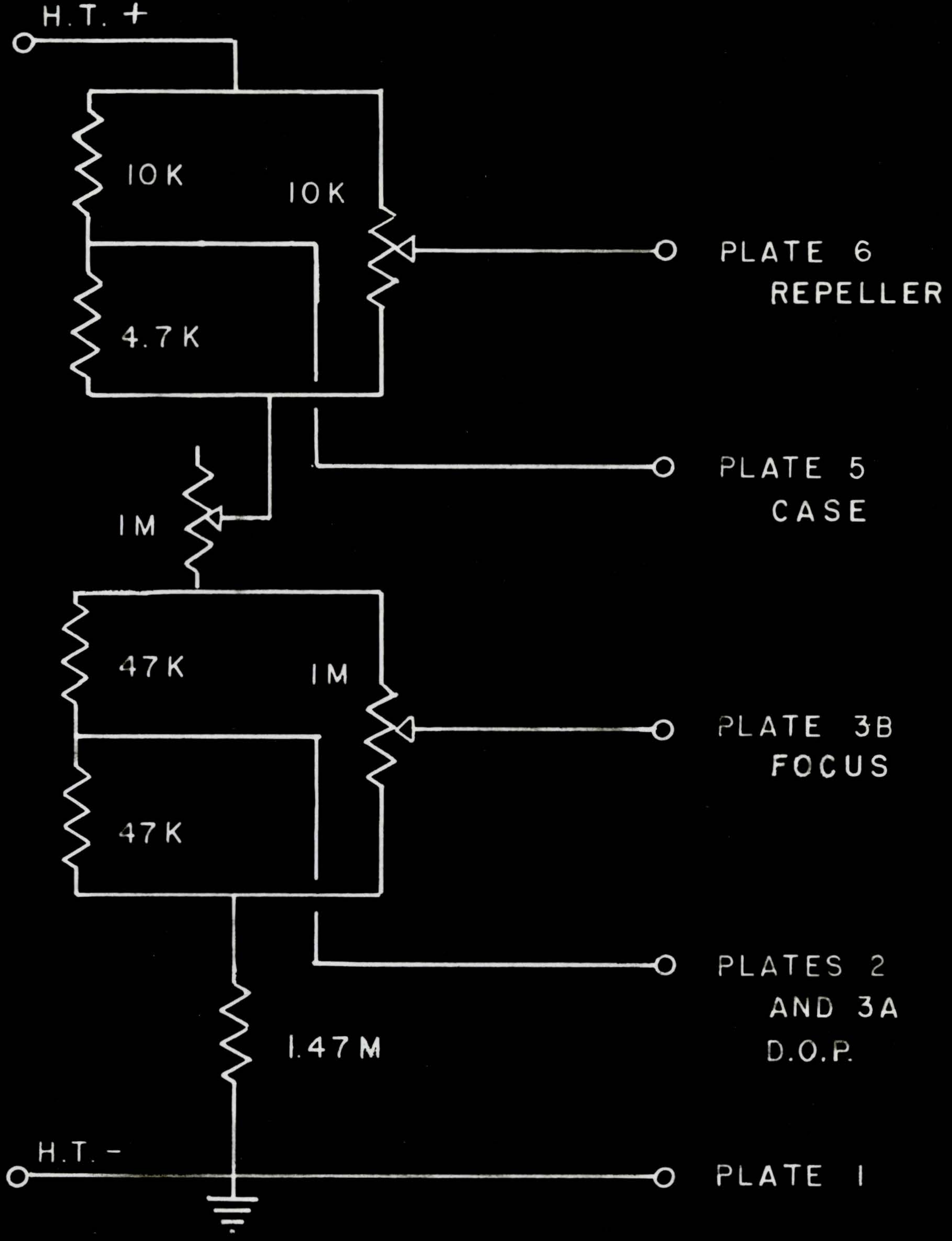
As water absorbs sulphur dioxide, every attempt was made to remove it from the walls of the combustion train by flaming and from the source material. If the troilite was found to contain moisture, it was roasted at 500° C for 15 minutes in an atmosphere of nitrogen.

Previously, carbon dioxide in the sulphur dioxide had been removed by freezing down the sulphur dioxide in a bath of dry ice and acetone and pumping off the gas that remained. However, at this temperature -85° C sulphur dioxide has a vapour pressure of 0.5 centimeters and thus some always was lost. This loss resulted in a small but significant fractionation of the sulphur isotopes. Since most of the troilite samples were reasonably free of carbon impurities, the carbon dioxide content of each sample was not large enough to cause trouble in the mass spectrometer, and no attempt was made to remove it.



ION SOURCE ASSEMBLY

FIG IV



POTENTIAL DIVIDER CIRCUIT

FIG V

Sea Water Sulphates

The sea water sulphates were prepared for analysis by Dr. Rudolph Wallouch.

The sulphates were precipitated from the water as barium sulphate, then reduced by digestion with a mixture of hydriodic, hydrochloric, and hypophosphorous acids. Hydrogen sulphide was evolved, bubbled through distilled water to remove the hydrogen chloride fumes and bubbled into a cadmium acetate solution. The heavy yellow cadmium sulphide was immediately converted into silver sulphide. By the same method as described earlier for troilite, the silver sulphide was converted to sulphur dioxide.

Mass Spectrometry

The mass spectrometer was essentially the one described by Wanless and Thode (52). It is a conventional 90 instrument modified to permit simultaneous collection and measurement, by means of a null method, of ion currents due to masses 64 and 66. A magnetic valve system is used to facilitate switching from the standard gas to the unknown. The collector assembly is constructed so that only the ion currents of masses 64 and 66 strike the collector electrodes; all contributions of other masses are eliminated.

Since the above mentioned work, the source assembly has been modified in order to increase its efficiency. A repeller plate which sits above the ionization chamber has been added (see Figure IV). The wiring of the output circuit from the high voltage supply has been changed as in Figure V so that the voltage on this plate can be varied from 2.25 volts above to one volt below the accelerating voltage. The rest of the assembly remains unchanged. The drawing-out potential applied between plates 2 and 3A can be varied from 1500 to 900 volts. Plate 3B is used as a focus control and can be changed by 25 volts above and below the accelerating voltage while the ions are accelerating plates 2 and 1.

Formerly a direct-current inverse feedback amplifier was used to amplify the ion beam due to mass 64. However, this type of amplifier was found to be troublesome because of its lack of stability. It has been replaced by a Vibrating Reed Electrometer (Model 30, Applied Physics Corporation), the output of which is fed across 1650 ohms, the required external output circuit resistance. The external resistance is made up of 650 ohms in series with a 10,000 ohm put-and-take potentiometer paralleled by 1111 ohms.

Since the equations previously used to find the sizes of the grid leaks, do not hold for this type of amplifier, R_1 and R_2 had to be found by trial and error. They were chosen such that when the two ion beams were balanced, the moving contact on the potentiometer was at the centre position. R_3 was chosen so that the sensitivity would be about six centimeters displacement per one percent difference between standard and unknown gas. It turned out that the desired conditions were achieved with $R_1 = 10^9$ ohms, $R_2 = 10^{10}$ ohms, and $R_3 = 10^{10}$ ohms (Victoreen Hi-Megohm Resistors).

The last change made in the mass spectrometer was the replacing of the Leeds and Northrup recorder by a Brown 1/2 second recorder (Minneapolis Honeywell Instrument Co.). While this required no major changes it was necessary to construct a simple battery and potentiometer circuit to provide a constant input voltage to hold the pen at the centre of the chart as required for simultaneous collection. The Leeds and Northrup instrument possessed an internal test voltage circuit that was used for this purpose.

Analytical Procedure: The output voltage created by the ion current at mass 64 was used as reference voltage and kept the same for both standard and unknown gas samples. This was done by adjusting gas pressures for identical 64 peak heights on single collection. With the standard sulphur dioxide flowing into the instrument and the instrument switched to simultaneous collection, the put-and-take potentiometer was moved to the position where the recorder indicated that a balance between ion currents 64 and 66 had been achieved. The sensitivity of the mass spectrometer was then determined by finding the amount of displacement of the recorder pen from its central position in terms of the percentage difference between two settings of the put-and-take potentiometer. This calibration was done before and after each run.

When the unknown gas sample flowed into the instrument, the balance was destroyed by the change in intensity of the 66 ion beam, the 64 beam being constant. This change created a displacement of the recorder pen and the size of this was directly proportional to the variation in the 64/66 ratio of the unknown compared to the standard gas. Since the standard has a known 64/66 value, the 64/66 ratio of the unknown could be calculated by comparing its displacement to the displacement created when the put-and-take was moved to a new position in the calibration. For example, assume that the calibration had revealed a one centimeter shift for 0.2 percent difference in isotopic abundance and the pen moved six centimeters when the unknown gas was admitted to the instrument. Then the percentage difference between 64/66 ratios of the two gases is 6/1 x .2 = 1.2 percent and the increment of difference is 20.236 x 1.2/100 = .243 where 20.236 is the 64/66 ratio of the standard. The increment is either added to or subtracted from 20.236 depending on whether the pen shifted to the left (a depletion of S^{34}) or to the right (an enrichment in S^{34}) of the central position. This value then is the 64/66 ratio of the gas under analysis.

The ion beam at mass 64 is made up of $S^{32}O^{16}O^{16}$ while mass 66 is composed of $S^{32}O^{16}O^{18}$, $S^{34}O^{16}O^{16}$, $S^{32}O^{17}O^{17}$, $S^{33}O^{16}O^{17}$. The last two contribute very little to this beam and can be neglected. Thus,

$$\frac{64}{66} = \frac{S^{32}O^{16}O^{16}}{S^{34}O^{16}O^{18} + S^{32}O^{16}O^{18}}$$

$$= \frac{1}{2\,\frac{O^{18}}{O^{16}} + \frac{S^{34}}{S^{32}}}$$

The value of O^{18}/O^{16} in the oxygen used to burn the samples was taken as 0.00208 as previously determined. Hence,

$$\frac{32}{34} = \frac{1}{66/64 - 0.00416}$$

Once the 64/66 ratio for the unknown gas was determined the value was substituted in the above and the desired S^{32}/S^{34} ratio obtained. By this procedure, relative isotopic abundances were determined with a precision of 0.02 percent.

RESULTS AND DISCUSSION

Results - Meteorites

Thode and Macnamara (40) reported in 1950 the results of studies carried on with the sulphur found in meteorites. They examined ten samples, eight siderites (iron), one aerolite (stony) and one siderolite (stony-iron) and found that the S^{32}/S^{34} ratios were remarkably constant.

Because of the increased precision of the simultaneous collection mass spectrometer over the conventional variety it was felt that small variations in isotopic abundance of the sulphur might make themselves apparent if the above mentioned samples were re-examined. Seven of the old meteorites and eleven new samples have been analysed, while one from the old group "Beenham" Union County, New Mexico, has been taken as standard with 22.200 as the S^{32}/S^{34} ratio. In all, eighteen meteorites, thirteen siderites, one siderolite and four aerolites have been studied. The new results are tabulated in Table I, while Table II compares the present with the old values.

In order to make sure that no fractionation had occurred in the preparation of the sulphur dioxide from the source material, nine samples of sulphur dioxide from the troilite of Bella Roca, Mexico, were prepared on different days. These results are listed in Table III. As it can be seen from Table IV, the mean deviation of the results obtained by running the same sample in the mass spectrometer ten times over a period of two months is 0.003. The mean deviation of the nine preparations from the same troilite is 0.001. This indicates that any number of sulphur dioxide samples could be prepared from the same material and each sample would give the same value for the S^{32}/S^{34} ratio within the limits of the instrument. Hence, the isotope ratio differences between standard and unknown gas were determined to within 0.02%, the precision of the mass spectrometer.

Of eighteen meteorites examined, sixteen have been found to have identical sulphur isotope abundances within 0.02 percent, the precision and accuracy of the present determination. Previously, Thode and Macnamara (40) had analysed eleven samples and found the abundances to be the same within 0.1 percent. However, two samples are depleted in S^{34} relative to the average of the sixteen by a significant amount. These two are among four or five fragments which showed no visible troilite and had to be pulverized to a fine powder. Because of the low sulphur content of these two specimens of meteorites, a large amount of the powders had to be used to get sufficient sulphur dioxide for analysis. Perhaps in the grinding of the fragments, a chemical reaction took place which caused fractionation of the sulphur isotopes or some impurity added to the material that would cause the difference. In any case, more of these meteorites must be obtained and studied before the results can be taken as conclusive.

Results - Sea Water

The isotopic composition of the sulphates in sea water was compared to that of meteoritic sulphur from "Beenham," Union County, New Mexico, whose S^{32}/S^{34} ratio was taken as 22.200. Samples of water from the Pacific and Arctic oceans were analysed previously and of these analyses, the results of four were published (53). Because of the increased sensitivity of the simultaneous collection mass spectrometer, it was felt that these samples should be reanalysed. Other samples were obtained from the Atlantic and included in the survey. The results are tabulated in Tables V and VI.

The sea water sulphates, following the general pattern of sulphates, were enriched in the heavier isotope. The maximum spread in S^{34} content was 0.039 percent, the most enriched sample was from 13°00'N, 38°58'W Pacific Ocean and the most depleted sample from Sanwich Inlet.

Samples from Halifax Harbour and Resolute Bay analysed previously, were thought to be especially enriched. While another specimen could not be obtained from Halifax Harbour, several samples of Resolute Bay water were secured and the average of all measurements taken for the final result. The S^{32}/S^{34} ratio for each such sample showed only the fluctuations in value that could be expected to result from small daily changes in the instrument. The average so arrived at was 21.839, compared with the previously reported value of 21.73. From this it is reasonable to conclude that the value of the S^{32}/S^{34} ratio for Halifax Harbour is also in error, showing too great an enrichment in S^{34}.

Certain samples previously reported as being depleted in S^{34} (54), i.e., Pacific Ocean 31°49.5'N 125°58'W at 2500 meters depth when reanalysed were found to have a slightly greater enrichment in the heavy isotope than previously realized. The old value for the isotopic composition was 21.97 while the new value is 21.832.

The differences between the old and new results are greater than 0.1 percent, the precision of the previous measurements. It is thus reasonable to assume that a wrong standard was used as comparison in the earlier work. Another possible explanation is that in the chemical recovery, all the sulphate in the original preparation was not obtained and consequently the sulphur isotopes were fractionated during the reaction.

The samples taken from six different spots in the Atlantic at three different depths have an average ratio of 21.805. A similar group of samples for the Arctic and Pacific give an average S^{32}/S^{34} ratio of 21.833. While the difference between the two results is small, there seems to be a slight but significant enrichment in S^{34} in the sulphates from the Atlantic.

Discussion - Meteorites

From Figure I, it is clear that meteorites have S^{32}/S^{34} ratios near the average for the samples of terrestrial sulphur so far studied. This would suggest that at the time of the earth's formation, the isotopic composition of the sulphur was that now found for meteorites. From that time, and especially from about eight hundred million years ago, terrestrial sulphur has been fractionated by geological and chemical processes. This has spread the S^{32}/S^{34} values above and below the meteoritic base level. Since the meteorites do not show large variations in isotopic abundances, it can be concluded that they have undergone no such reactions. These results are also consistent with the view now generally accepted that meteorites originated from within the solar system.

Several other studies on the isotopic content of various elements in meteorites also lead to this conclusion. Brown and Inghram (55) could find no difference within the limits of detection in the Cu^{63}/Cu^{65} ratio between two samples of meteoritic and terrestrial copper. Similarly, Valley and Anderson (56) found two terrestrial and twelve meteoritic iron specimens identical. Nine samples of igneous rock were examined by Silverman with regard to the oxygen isotope composition and it was discovered that they were 0.65 to 0.85 percent enriched in O^{18} compared to Hawaii sea water. Since these rocks were formed at high temperature, their oxygen isotope concentrations are expected to be uniform and to represent the primordial composition. He then examined several meteorites using the same standard and found a 0.65 percent enrichment in the heavy isotope. These results, including the new sulphur data, indicate that our planet and meteorites are related in some manner.

Discussion - Sea Water Sulphates

The sea water samples obtained from the central Atlantic represent water from that part of the ocean which is close to the boundary between Northern Central and Southern Central water; no Equatorial water mass exists in the Atlantic. The most northerly of these specimens would perhaps be wholly Northern Atlantic water, while the southern ones would be a mixture of both. Through this region travelling from east to west, is the Northern Equatorial Current having a surface temperature throughout the year of 20° - 25° C. At a depth of four hundred meters the temperature drops to 8° - 11° C. The samples from the Pacific Ocean were taken from the California Current, a wide body of water travelling rather sluggishly to the southeast. The temperature of the surface water in this region is 9° - 20°C in the summer and 5° - 8° C at a depth of 400 meters.

Variations in the isotopic constitution of sulphur in the ocean water were noted for various positions from which the water was taken. If any process was occurring in the ocean involving sulphur isotopes, it might be expected that as the temperature decreased, the concentration of the heavy isotope would increase in the sulphate. Since, in the regions where the sulphates were obtained, the temperature decreases with depth, a temperature effect might appear as a depth effect as well.

However, the variations in the S^{32}/S^{34} content of these specimens at the various depths appear to be random and small. In fact, these sulphates possess as constant an isotopic composition as any group of sulphur samples yet examined with the exception of the meteoritic sulphur.

Recently, Kulp (58) has studied the behaviour of C^{14} in the organic material in the deeper parts of the ocean. He calculates that these deposits are on the average, approximately two thousand years old, suggesting that the oceans become completely mixed every five thousand years. This would mean that the sulphates in the ocean water also become mixed and even if some localized enrichment of the sulphate occurred, the mixing would soon obliterate the effect. From this point of view an explanation is obtained for the remarkably constant S^{32}/S^{34} ratios found for sulphates of the sea.

As mentioned earlier, previous to eight hundred million years ago, the biological sulphur cycle in the sea was probably not operating and the isotopic composition of terrestrial sulphur was probably very close to that now found for meteoritic sulphur and igneous rocks. Since that time the cycle has become active and the sulphur isotopes have been fractionated at an ever increasing rate. Thus, the isotopic abundances of the sulphates in the sea and the sulphides from them by means of the cycle would gradually be changing with time. It would appear from the above results that at any one time the isotopic composition of the sulphates is relatively constant over all the oceans and at all depths. As the sulphides and sulphates are deposited from the sea in the form of sedimentary rock, the isotopic content should be relatively constant regardless of the position on the earth where the rock was laid down. Consequently, the governing factor in the S^{32}/S^{34} ratio of sulphur in such rock is not position but time.

TABLE I

ISOTOPIC DISTRIBUTION OF SULPHUR IN METEORITES

Name	Type	Present S^{32}/S^{34} Ratio	
Bella Roca Mex.	Siderite	22.230	± 0.003 †
Bear Creek, Colo.	Siderite	22.227	"
Cambria, N. Y.	Siderite	22.230	"
Jose Wright Mtn.	Siderite	22.215	"
Duchesne	Siderite	22.222	"
Duchesne	Siderite	22.222	"
Wichita Co. Kans.	Siderite	22.227	"
Waterville	Siderite repeat	22.227 22.228	"
Canyon Diablo	Siderite	22.222	"
Canyon Diablo	Siderite	22.212	"
Canyon Diablo	Siderite	22.220	"
Canyon Diablo	Siderite	22.227	"
Cumpas		22.227	"
Brenham Co. Kans.	Siderolite	22.232	"
Indarch	Aerolite	22.212	"
Hugoton, Kans.	Aerolite	22.222	"
Gladstone N. Mex.	Aerolite	~~22.280~~ 22.232	"
Alamogordo, N. Mex.	Aerolite	~~22.241~~ 22.222	"

† Mean Deviation

TABLE II

COMPARISON OF PRESENT RESULTS WITH THOSE OF PREVIOUS WORKERS

	Present S^{32}/S^{34} Ratio		Old S^{32}/S^{34} Ratio	
Canyon Diablo	22.222	± 0.003+	22.21	± 0.002+
Canyon Diablo	22.220	"	22.22	± 0.02
Canyon Diablo	22.220	"	22.21	± 0.02
Canyon Diablo		"	22.21	"
Canyon Diablo	22.227	"	22.21	"
Waterville	22.227	"	22.20	"
Duchesne	22.222	"	22.24	"
Duchesne	22.222	"	22.23	"
El Loba Argentine			22.22	"
Brenham Kansas	22.232	"	22.23	"
Union Co. N. Mex.			22.20	"

+ Mean Deviation

TABLE III

SAMPLES MADE FROM SAME MATERIAL TO FIND REPRODUCIBILITY OF METHODS OF PREPARATION

Troilite from Bella Roca Mexico

Date Prepared	S^{32}/S^{34} Ratio
April 1	22.227
April 1	22.232
April 1	22.232
April 1	22.227
April 28	22.227
April 28	22.237
July 31	22.232
July 31	22.225
August 1	22.232
Average	22.230 ± .001†

† Mean Deviation

TABLE IV

COMPARISON OF RESULTS OBTAINED WITH SIMULTANEOUS COLLECTION OVER A PERIOD OF TWO MONTHS

Date	S^{32}/S^{34} Ratio
December 5	22.207
December 5	22.198
December 9	22.193
December 9	22.203
December 30	22.198
December 31	22.202
January 7	22.198
January 13	22.202
January 15	22.198
January 16	22.198
Average	22.200 ± 0.003[†]

[†] Mean Deviation

TABLE V

SULPHUR ISOTOPE ABUNDANCES FOR SEA WATER SULPHATES FROM THE ATLANTIC

Position and Date Collected	Depth (Meters)	S^{32}/S^{34} Ratio	
22°00'N 30°00'W	10	21.796	± 0.003[†]
Feb. 14, 1952	683	21.808	"
	1213	21.851	"
09°25'N 20°15'W	1	21.801	"
Feb. 28, 1952	700	21.777	"
	1553	21.806	"
13°00'N 38°58'W	23	21.780	"
March 4, 1952	651	21.772	"
	1600	21.844	"
16°24.5'N 38°53.5'W	21	21.851	"
March 31, 1952	636	21.791	"
	1432	21.796	"
16°00'N 46°08'W	24	21.839	"
April 2, 1952	975	21.796	"
	1838	21.780	"
11°59'N 56°03'W	43	21.820	"
April 9, 1952	670	21.812	"
	1615	21.818	"

[†] Mean Deviation

TABLE VI

SULPHUR ISOTOPE ABUNDANCES FOR SEA WATER SULPHATES IN THE PACIFIC AND ARCTIC

Position	Depth (Meters)	S^{32}/S^{34} Ratio Macnamara	S^{32}/S^{34} Ratio New Results
Resolute Bay, N.W.T.	Surface	21.73 ± 0.02†	21.838 ± 0.003†
39°23'N 129°55'W	Surface	21.84 "	21.820 "
	2500	21.88 "	21.801 "
25°31'N 119°46'W	Surface	21.90 "	21.842 "
	2500	21.89 "	21.830 "
Pacific Naval Lab #27	180	21.80 "	21.837 "
Sanwich Inlet			21.856 "
Halifax Harbour N.S.		21.70 "	

† Mean Deviation

SUMMARY

Meteoritic sulphur and sea water sulphates were studied with regard to their sulphur isotope abundances. Sulphur from eighteen meteorites was analysed, sixteen samples of which had the same S^{32}/S^{34} ratios within 0.02 percent the precision and accuracy of the determinations. Since the average isotopic composition of terrestrial sulphur is very close to that found for meteorites, it would appear that the sulphur in meteorites is the primordial sulphur. Further evidence is thus advanced for the theory that the earth and meteorites are related in some manner.

The sea water sulphates were obtained from various depths in the Atlantic, Pacific and Arctic Oceans. The isotopic composition of the sulphates had an overall variation of 0.39 percent and were enriched in S^{34} relative to the meteoritic base level. From these results, it can be concluded that the sulphates in the sea are uniform in their isotopic composition today, and have probably been uniform throughout time, even though S^{32}/S^{34} ratio has been gradually changing.

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